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13. ABSTRACT (Maximum 200 words) In this work we have studied the properties of Rydberg states of amines and ethers with a view to their application to and importance for the chemistry of energetic materials. We have learned that in clusters these Rydberg states can be quite reactive and, in fact, they dominate the excited state chemistry and dynamics through electron transfer reactions. This unexpected and new phenomenon can be understood based on available excited state orbitals (Rydberg, $\sigma^*$ , $\pi^*$ ) for the solvent molecules. If the solvent molecule for the amine or ether is another amine, ether, or aromatic, a low lying electron transfer state is generated, due to the exchange interaction, which is the first step in a chain of chemical reactions. We conclude that these electron transfer states generated from Rydberg state-solvent interactions are quite general and can represent the initial step in electron transfer oxidation-reduction chemistry for energetic materials. <b>DTIC QUALITY INSPECTED 5</b>				
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1. *ETHERS.* Our main thrusts for the initial part of our studies of highly excited electronic states energetic materials are to observe Rydberg spectra of new model systems and of clusters. Both aspects of this work have been highly successful. We have obtained cluster spectra of 1,4-dioxane with Ar, Kr, CH<sub>4</sub>, CD<sub>4</sub>, CF<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>12</sub>, C<sub>6</sub>D<sub>12</sub>, SiH<sub>4</sub>, and Si(CH<sub>3</sub>)<sub>4</sub>. We have also calculated the structure and van der Waal vibrational modes of these clusters. These studies can be summarized as follows.

One-color 2 + 1 multiphoton mass resolved excitation spectra are obtained for molecular Rydberg spectra of 1,4-dioxane clustered with nine non-polar solvents. These spectra can be analyzed in terms of calculations which model the minimum energy cluster geometry and the van der Waals (vdW) normal mode frequencies for these structures. The results show that, as the solvent becomes more complex, so do the cluster spectra and calculated structures. For 1,4-dioxane clustered with Ar and Kr, the model calculations indicate that two cluster geometries exist, in good agreement with spectral results. Comparable results are obtained by a similar analysis of the 1,4-dioxane(CH<sub>4</sub>)<sub>1</sub> cluster spectra. In this case, computer simulations find three stable cluster geometries, two of which have analogous structures and binding energies to those found for dioxane clustered with Ar and Kr, and a third which is less stable. These conclusions are also confirmed by the deuteration of methane which facilitates the discrimination of transitions resulting either from vdW modes or from different cluster geometries. These results show that, for this system, empirical potential energy calculations provide a reasonable model for cluster geometries and intermolecular vdW modes. An exception to this is the apparent inability of the employed harmonic potential to model very low frequency intermolecular motions as seen in the 1,4-dioxane(CH<sub>4</sub>)<sub>1</sub> cluster spectrum. For 1,4-dioxane clustered with ethane, broad features appear in the spectrum which are assigned to multiple cluster geometries based on the cluster geometry simulations and the magnitude of the calculated vdW normal mode frequencies. This trend then

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continues, with the molecular Rydberg spectra becoming more congested for dioxane clustered with propane, silane, tetramethylsilane (TMS), and cyclohexane.

An upper limit for the cluster binding energy may be determined from the energy at which cluster signal vanishes and the cluster spectral shift. These maximum binding energies are approximately  $100\text{--}300\text{ cm}^{-1}$  greater than calculated binding energies. This reflects the relative efficiency at which a sufficient amount of excess vibrational energy may relax into the reaction coordinate for intermolecular dissociation.

For all of the clusters, the electronic origins are blue shifted with respect to the bare 1,4-dioxane origin. The spectral shift for a cluster can be viewed as the difference between the ground and excited state binding energies. Therefore, the observed blue shift indicates that the cluster is destabilized upon excitation into its molecular Rydberg state. This is consistent with the model in which the excited state intermolecular potential becomes repulsive due to the increased radial distribution of the excited electron in the Rydberg state.

In addition to these cluster studies with dioxane, we have also obtained new Rydberg spectra for diethyl ether, tetrahydrofuran (THF) and methyl vinyl ether, diisopropyl ether. These spectra are very rich in structure and sharp, potentially revealing a great deal of information about the Rydberg states of many molecules. Spectra are obtained by 2-color multi-photon processes so fragmentation is controlled.

Two photon resonance enhanced multiphoton ionization spectra are obtained for the (n,3s) Rydberg transition of diethyl ether-h<sub>10</sub>, diethyl ether-d<sub>10</sub>, diisopropyl ether, and methyl vinyl ether in a supersonic jet expansion. A low frequency progression is resolved for diethyl ether and diisopropyl ether. The intensities and transition energies of this progression are nicely reproduced by fitting to a polynomial potential truncated at the quartic term. The analysis leads to the conclusion that the progressions are a result of a change in ether geometries along the antigeared torsional coordinate upon excitation. The difference between the ground and excited state potential energy surfaces can be interpreted as a change of nonbonding interactions between the oxygen 2p lone pair electrons and the  $\beta$ -methyl group upon excitation of a 2p electron to the diffuse 3s molecular Rydberg orbital.

2. *AMINES*. Two color, 1+1 and 2+1, mass resolved excitation spectroscopy (MRES) is used to obtain molecular Rydberg ( $3s \leftarrow n$ ) spectra of azabicyclo [2.2.2] octane (ABCO) and diazabicyclo [2.2.2] octane (DABCO) clustered with argon. Laser/nozzle timing delay studies are employed together with time-of-flight mass spectroscopy to identify cluster composition. Population depletion experiments are used to discriminate between clusters with the same mass, but different geometries. A Lennard-Jones 6-12 potential is used to model the intermolecular interactions and predict minimum energy cluster geometries and cluster binding energies. The

experimental results are combined with the cluster geometry calculations to assign spectral features to specific cluster geometries. Three excited state potentials are proposed to model the experimentally observed line shape, spectral shift, and cluster dissociation. The relationship between these model potentials and the cluster binding sites suggests that the form of the cluster intermolecular potential in the Rydberg excited state is dictated by the distance between the argon and chromophore atoms. A comparison of results for ABCO(Ar)<sub>1</sub> and DACO(AR)<sub>1</sub> leads to the conclusion that the nitrogen 3s Rydberg orbital in clusters of DABCO is delocalized.

We have shown that clusters of ABCO and DABCO with rare gas atoms, N<sub>2</sub>, saturated linear ( $n = 1, \dots, 7$ ) and cyclic (C<sub>6</sub>H<sub>12</sub> and CH<sub>3</sub>C<sub>6</sub>H<sub>11</sub>) hydrocarbons have repulsive interactions in their Rydberg state. This is obvious from the large blue shift observed for these transitions and the associated cluster fragmentation. Heavier rare gas atoms such as Kr reduce the excited state lifetime of the Rydberg state of the cluster (from  $\sim 4 \mu\text{s}$  to  $< 1 \mu\text{s}$ ) and generate a very long lived bare molecule signal in the ABCO or DABCO mass channel. We attribute the long lived state to the triplet 3s Rydberg state and the generation of the bare molecule to cluster fragmentation. The triplet state is  $\sim 600 \text{ cm}^{-1}$  lower in energy than the singlet state and the additional excess triplet vibrational energy causes the cluster to fragment. Thus, even for simple clusters the Rydberg state is very reactive in the presence of solvent.

Second, if these caged amines are solvated by unsaturated hydrocarbons, such as benzene, ethylene, toluene, or polar molecules such as amines, acetonitrile, ethers, thioethers, the Rydberg transition is red shifted. Two reasons for this can be identified: dipole induced dipole interactions and electron transfer interactions. Again, lifetime studies show here that following cluster excitation to the 3s Rydberg state, an electron transfer state evolves and has a very long lifetime for amine and ether clusters. We can show that these dynamics are very different than those characterized for clusters that intersystem cross to the triplet state. The electron transfer state is very stable and the cluster has a very large binding energy in this state.

Both triplet and electron transfer behavior show the highly reactive nature of Rydberg state clusters: these states should play an important role in the chemistry of energetic materials both in the gas phase and in condensed phases.

3. *MORE COMPLEX MATERIALS.* Supersonic jet laser spectroscopy has been employed to study molecular Rydberg states of compounds related to energetic materials. In the past year we have continued our studies of amines and ethers to determine electron transfer reactions, triplet state generation and ionization properties. Specific systems include the ones depicted below (Figure 1). The hydrocarbons are used to show how the properties of these systems change with heteroatom inclusion.

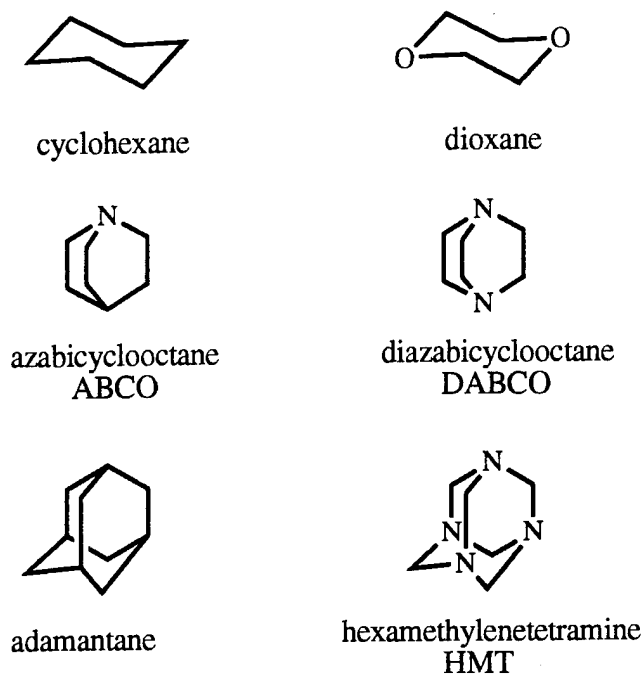


Figure 1

We have recently begun to expand the systems of study to include various single ring systems with nitrogen nitrogen bonds and some aromatic heterocycles. The 3s Rydberg states are found for pyridine, pyrazine, pyrimidine, and pyridazine. We are presently investigating the 3s Rydberg states of the saturated ring systems given in Figure 2. Additionally, the substituted amines  $R_3N$  ( $R=CH_3, C_2H_5, C_3H_7$ ) are very important compounds for the dissociation reaction of RDX and HMX. We have data now for  $CH_3NH_2$ ,  $C_2H_5NH_2$  and  $(CH_3)_2NH$ . The importance of these systems lies in their ionization and fragmentation behavior as they are models for what happens to energetic materials at high energy and in the ionic state.

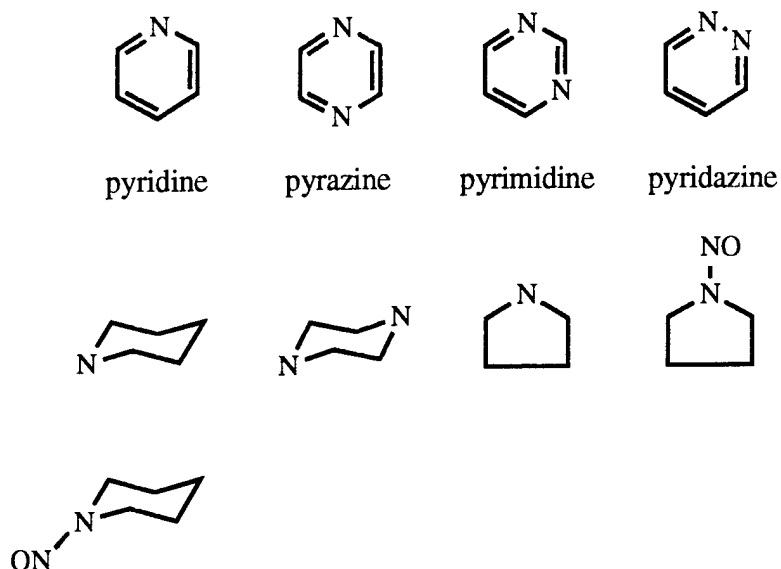


Figure 2

Monocyclic amines and alkane-substituted ammonias are model compounds for energetic materials; their excited state dynamics, energy levels, Rydberg states, and chemistry should be useful information for the unraveling of the complex excited state dynamics and chemistry of energetic materials. In this past year, we have been studying the excited state behavior of methylamines  $[(CH_3)_x H_{3-x} N]$ , ethyl amines  $[(C_2H_5)_x H_{3-x} N]$ , and the mono- and di-azabenzenes. We are presently in the process of writing up these studies and finishing the last few details of this effort.

The low  $2p3s \leftarrow (2p)^2$  Rydberg transitions for the azabenzenes are surprisingly unknown considering the years over which they have been studied. Our spectra of pyridine, pyrazine, pyrimidine, and pyridazine show important systematics to the extent that we are able to eliminate a number of misassigned features for pyridazine and pyrimidine. The systematics of the spectral features for this series seem to indicate that the interaction between the lone pair electrons is not the dominant factor in determining the transition energies. Theoretical studies of the excited states of pyrazine also show that the lone pairs are localized but that the Rydberg states are delocalized. We are just completing new calculations for pyrazine at the CASSCF/MBPT2 (complete active space self-consistent field/many-body second order perturbation theory) level which show these effects and which include dynamic correlation energy to the state-of-the-art extent. In the next few months we will complete these calculations and be able to make important correlations between Rydberg state theory and experiment.

Similar studies have been completed for the methyl- and ethyl-substituted amines. We have complete H/D isotope substitution spectra for  $CH_3NH_2$  and spectra of all the other systems now. The previous assignments of these spectra are not correct. Two electronic transitions have been

identified in these spectra, and both were assigned as Rydberg states. The theoretical calculations show that the lower energy state is not a Rydberg state but a valence state that is completely delocalized over the system. This accounts for its reactivity. The agreement between our new spectra, obtained on cold isolated systems for the first time, and theory is excellent.

The reactivity of the excited states of the above amine seems to have been underestimated previously because of the assumed localization of these states and the misunderstanding of their orbital composition.